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EFFECTS OF HYDROTHERMAL EXPOSURE ON A LOW-TEMPERATURE CURED EPOXY

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ABSTRACT

Thermal mechanical analysis was employed to monitor the penetration temperature of a low-temperature epoxy resin (EPON 826/D230). Both neat resin and E-glass composite samples were examined. The effects of cure temperature variation and moisture content on the apparent glass transition temperature were determined.

INTRODUCTION

The purpose of this study was to investigate the effects of cure temperature variation and moisture content on the glass transition temperature, T_g , of a low-temperature, aliphatic amine cured epoxy. It is well known that T_g of an epoxy resin varies with extent of cure of the resin. Hence, it is necessary to determine the extent of cure as a function of time and temperature to ensure that optimal cure is attained. The glass transition temperature can also vary as a function of moisture content in the resin. Depression of T_g due to absorbed moisture is characteristic of epoxy resins and is particularly well documented for higher temperature epoxy systems (Ref. 1). It is desirable to determine the sensitivity of an engineering resin to moisture and to verify that the T_g cannot be depressed below the estimated upper use temperature of a component fabricated from the resin.

The resin employed in this study was Epon 826/D230. The resin has been used in the fabrication of a large, glass filament wound blade structure for the DOE/NASA wind turbine project (Ref. 2). The techniques and data discussed in this paper were developed as a preliminary part of a program to test selected specimens from the final composite blade.

EXPERIMENTAL

Reagents

Epon 826 is a commercial epoxy resin. It contains predominantly the diglycidylether of bisphenol-A. The resin was used without further purification. The resin was cured with Jeffamine D-230, a polyoxypropyleneamine of nominal molecular weight 230.

Sample Preparation

The reagents were used in the ratio: 30 parts amine per hundred parts epoxy by weight. This is, approximately, the stoichiometric mixture of the reagents. The resin was stirred for about 3 minutes before casting resin samples.

The composite samples were cut from a structure which had been wound and cured by the fabricator in approximately the same manner as the final blade (16 hr cure at 79⁰ C). The structure was wound with E-glass having a chrome-silane surface treatment. The composite contained nominally 60 weight percent glass. The samples contained voids, but were considered representative of the overall demonstration structure.

Moisture Exposure

Neat resin and composite samples were exposed to three different moisture environments: (1) 30 minute immersion in distilled

water at 100° C, (2) extended immersion in distilled water at ambient temperature (about 23° C), and (3) extended exposure in air at 100 percent relative humidity at ambient temperature. Samples were approximately 25 × 6 × 6 mm as exposed. Weight gains of exposed samples were determined after equilibrating the samples in ambient atmosphere for approximately 1 hour.

Instrumental Measurements

Thermal mechanical analyses (TMA) were performed using a commercial thermal analysis unit. A quartz penetration probe was employed with a probe tip having 2.54 mm diameter. The probe was loaded with a 10 gram weight. Neat resin samples were prepared in two ways. Bulk resin castings were cut into 6 × 6 mm squares at the available thickness (~3 mm) and measured directly. Samples cured at elevated temperatures were cast in standard aluminum differential scanning calorimetry (DSC) pans and were subsequently tested in the pans. The composite samples were sawed or sheared into approximate 6 × 6 × 6 mm cubes. Samples were loaded perpendicular to the fiber direction for expansion measurements and parallel to the dominant fiber direction for penetration measurements. DSC measurements were performed using a commercial thermal analysis unit.

RESULTS AND DISCUSSION

Extent of Cure

The resin undergoes partial cure at room temperature. The change in T_g with cure time is shown in Figure 1. Diglycidylether of bisphenol-A (DGEBA) epoxides cured with aliphatic amines typically exhibit glass transitions in the range 80° to 90° C (Ref. 3) and a similar T_g is observed for D230 cures (Ref. 4). Thus it is

evident that the resin does not cure completely at 23° C even after approximately 1 month. The resin is self supporting after about 2 days, but appears to be limited to a T_g of ~50° C when cured at 23° C.

Figures 2 and 3 show the change in T_g with cure times at elevated temperatures (60° and 80° C). As expected, the trend is similar to that of Figure 1. However, the samples approach higher limiting values of T_g , and the reaction occurs much more rapidly. The samples cured at 80° C approach a glass transition temperature of ~83° C which is the highest value of T_g observed in this study and is, approximately, the maximum T_g attainable with this epoxy/cure agent combination (Ref. 4). From these results it is evident that curing above room temperature is required to attain a glass transition temperature greater than 50° C. To attain complete cures (as indicated by maximum T_g) in a reasonable time, cure temperatures near 80° C are required. Studies (Ref. 4) have shown that curing at temperatures above 80° C does not result in higher T_g than the maximum discussed above. The cure schedule specified by the blade fabricator (16 hr at 79° C) appears adequate, but attainment of a complete cure is not certain.

The T_g data are presented for two thermal techniques: differential scanning calorimetry (DSC, Fig. 2) and thermal mechanical analysis (TMA, Fig. 3). The DSC data is, in general, believed to provide more accurate T_g values than the TMA data. This is due in part to stress relaxation in the loaded TMA sample which can cause premature probe movement. Indeed, the TMA data (Fig. 3) do give lower values of T_g at short times compared to the DSC data. However, the curves for the two techniques converge to the same T_g maximum for both cure temperatures at longer times.

Composite Analysis

While either DSC or TMA can be used for neat resin samples, highly filled resin samples do not give good results on the DSC due to the effective dilution of the resin in the sample. Because the glass fiber composite samples were of primary interest in this study, the TMA was employed for subsequent measurements. A comparison of two modes of TMA measurement are shown in Figure 4 (expansion mode in curve 1, and penetration mode in curve 2). The ordinate of the TMA plots defines relative vertical displacement of the loaded probe. Expansion is indicated by a positive slope of the curve (upward movement of the probe) while penetration is indicated by a negative slope of the curve (downward movement of the probe). The intersection of tangents on the thermal expansion curve and the softening point defined by intersection of tangents on the penetration curve both occur at approximately 75° C. This can be considered the apparent T_g of the sample (an as received sample of the demonstration structure). Fiber content, moisture content and other physical anomalies tend to broaden the glass transition temperature making it difficult to define the tangents to the curves used in determining the apparent T_g . In most composite samples (and even in wet, neat resin samples), the transition is so broad that an apparent T_g cannot be defined by tangents and used for comparison. As a result, the initial penetration temperature (shown in Fig. 4) was found to provide a convenient and conservative point for comparison. As will be seen below, this initial penetration temperature differs from the apparent T_g by less than 5° C for well defined penetration curves (see curve 2 in Fig. 5 and curve 3 in Fig. 6).

Effect of Moisture

As previously discussed, neat resin and composite samples were exposed to moisture in three ways: immersion in boiling water,

immersion in water at ambient temperature, and exposure to 100 percent relative humidity at ambient temperature. All three exposure conditions caused a weight gain of approximately 1.25 percent of resin weight (about 0.5 percent of composite weight). The effect of this moisture (apparent equilibrium content) on initial penetration temperature in neat resin and composites is shown in Figures 5 and 6.

Results for a single sample of the neat resin are shown in Figure 5 following sequential exposure to three different environments. The ambient temperature cured sample exhibited an initial penetration temperature of $\sim 50^{\circ}\text{C}$. One additional hour of cure at 138°C caused the penetration temperature (indeed, the apparent T_g) to reach its maximum, $\sim 83^{\circ}\text{C}$. Subsequent exposure to boiling water for 30 minutes caused the initial penetration temperature to decrease dramatically to approximately 58°C .

Figure 6 shows results for composite samples having four different hydrothermal histories. The complete history of the "as received" sample was not known, but it exhibited an initial penetration temperature of 65°C . After 178 days of exposure to 100 percent relative humidity at $\sim 23^{\circ}\text{C}$, the penetration temperature decreased to $\sim 58^{\circ}\text{C}$. The same decrease was observed for a sample immersed in water for a comparable time. A composite sample postcured for 1 hour at 138°C showed initial penetration at $\sim 78^{\circ}\text{C}$, and, as for the neat resin, exhibited a decrease in penetration temperature to $\sim 62^{\circ}\text{C}$ after 30 minutes in boiling water.

The trends in these data clearly show that the presence of nominally 1.25 percent moisture in this resin decreased the initial penetration temperature to less than 62°C in every instance. This temperature falls near the anticipated use temperature range for the blade. Because of the conservative values of apparent T_g determined in these experiments, it appears that the material should provide adequate performance in the intended

application. It must be kept in mind, however, that there are many other factors which could have deleterious effects on such a composite structure. For instance: (a) Unbalanced stoichiometry could lead to increased moisture uptake and increased depression of T_g . (b) Thermal spiking (freeze/thaw or rapid heating cycles) could cause increased moisture uptake due to cracking or crazing. Possibilities such as these make it imperative that adequate quality assurance procedures be instituted and maintained to provide a high initial T_g representative of a completely cured resin.

CONCLUSIONS

The effects of cure temperature variation and moisture exposure on Epon 826/D230 resin and composites has been examined. It was concluded that: (1) An elevated temperature cure is required to attain a resin T_g greater than 50°C . (2) A cure temperature greater than 80°C is required to increase T_g of the resin to its maximum in times less than about 12 hours. (3) The presence of about 1.25 percent moisture in the resin decreases its T_g to approximately 60°C .

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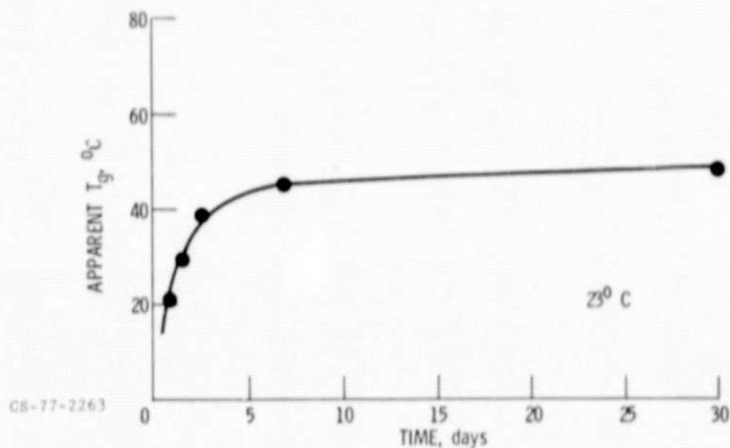


Figure 1. - Change in T_g (by TMA) of Epon 826/D230 as a function of time at ambient temperature.

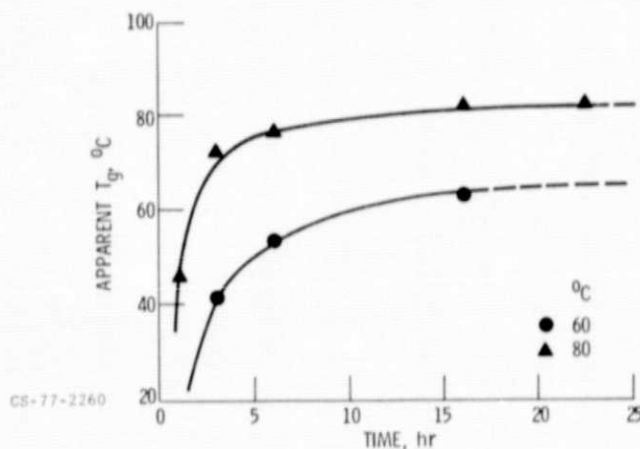


Figure 2. - Change in T_g (by DSC) of Epon 826 as a function of time at 60°C and 80°C.

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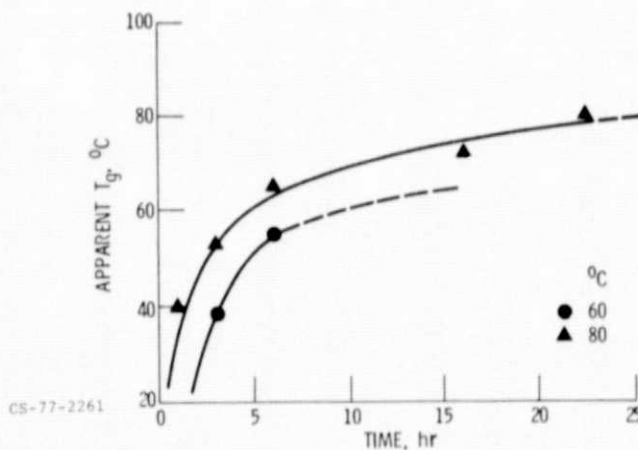


Figure 3. - Change in T_g (by TMA) of Epon 826/D230 as a function of time at 60°C and 80°C.

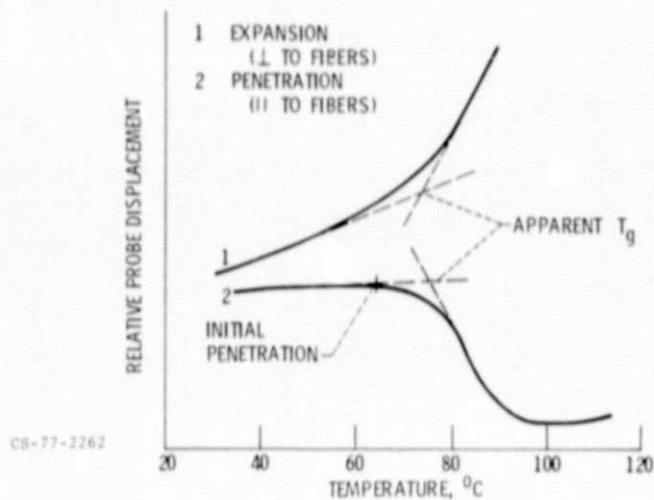


Figure 4. - Thermal mechanical analysis (expansion and penetration) of an E-glass/Epon 826/D 230 composite.

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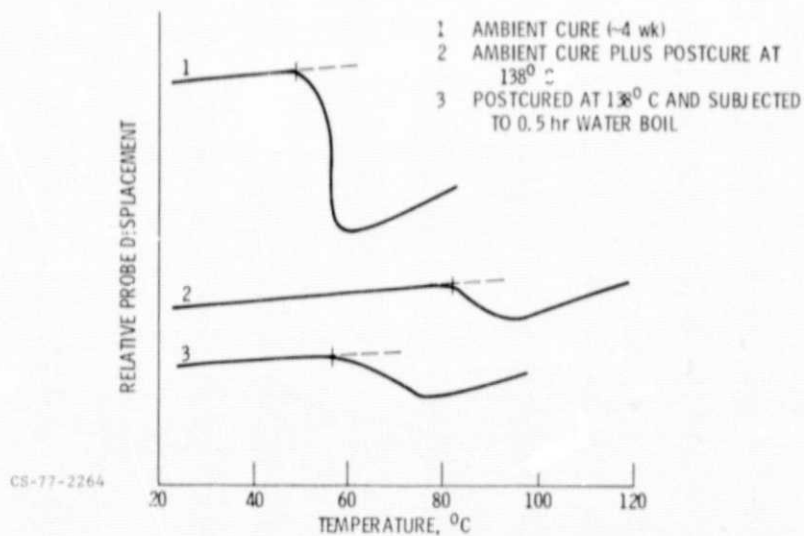


Figure 5. - Thermal mechanical analysis (penetration) of a neat resin sample of Epon 826/D230 after hydrothermal exposure.

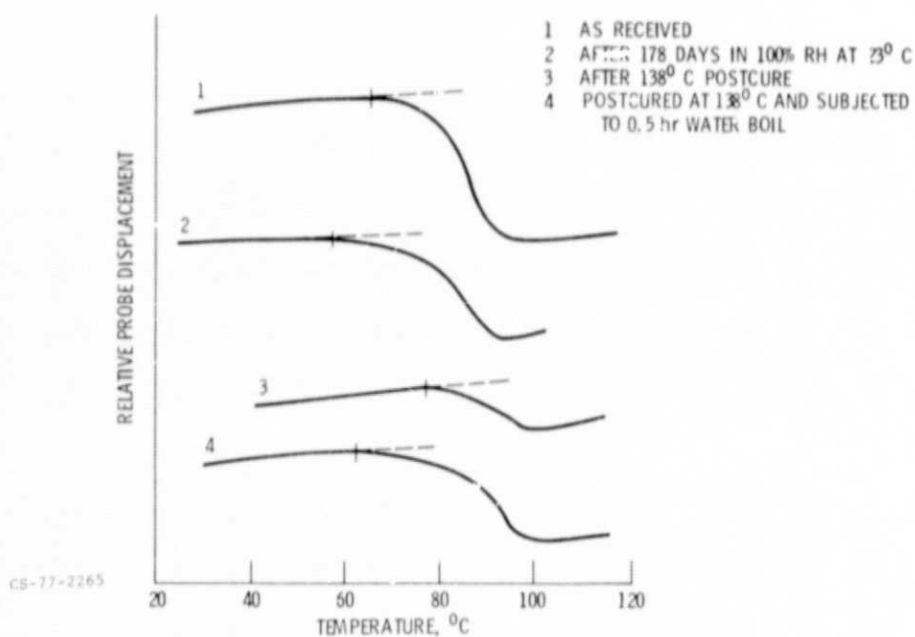


Figure 6. - Thermal mechanical analysis (penetration) of E-glass/Epon 826/D730 composite samples after hydrothermal exposure.